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K BASIN SPENT NUCLEAR FUEL CHARACTERIZATION

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Abstract: The results of the characterization efforts completed for the N Reactor fuel stored in the Hanford K Basins were collected and summarized in this single referencable document. This summary provides a "road map" for what was done and the results obtained for the fuel characterization program initiated in 1994 and scheduled for completion in 1999 with the fuel oxidation rate measurement under moist inert atmospheres.

Multiple sources of data input were frequently used to answer the two main questions which were the focus of the characterization efforts.

- What is the condition of the fuel elements stored in the two K Basins?
- How do the fuel elements behave under process conditions?

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EXECUTIVE SUMMARY

The results of the characterization efforts completed for the N Reactor fuel stored in the Hanford K Basins were collected and summarized in this single referencable document. This summary provides a "road map" for what was done and the results obtained for the fuel characterization program initiated in 1994 and scheduled for completion in 1999 with the fuel oxidation rate measurement under moist inert atmospheres.

Multiple sources of data input were frequently used to answer the two main questions which were the focus of the characterization efforts.

- What is the condition of the fuel elements stored in the two K Basins?
- How do the fuel elements behave under process conditions?

Budgets and schedule constraints dictated an attribute driven sampling to provide bounding behavior rather than a statistically based program. This report summarizes what was done and the results obtained to support the two main questions concerning the fuel. The data collected in some instances were rather limited due to the overall Spent Nuclear Fuel Project constraints.

The data used have not been fully reviewed in accordance with Office of Civilian Radioactive Waste Management (OCRWM) requirements. The results should, therefore, be used with caution.

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K BASIN SPENT NUCLEAR FUEL CHARACTERIZATION

1.0 INTRODUCTION

N Reactor fuel stored in the Hanford K Basins was characterized to provide baseline data for the Spent Nuclear Fuels (SNF) Project. The SNF Project's path forward to mitigate the safety concerns with continued storage of the degrading fuel in the K Basins requires data on the condition of the fuel in the K Basins and on how the material responds to the proposed process conditions necessary to place the SNF in long term storage.

The SNF Characterization Project was initiated in FY 1994 and will be completed in FY 1999. This report summarizes these examinations and provides a single source reference, or road map, to the detailed reports covering the characterization activities. This report summarizes what was done and the results of the corresponding examinations.

The number of elements collected from each basin were limited, i.e., 18 from K West and 9 from K East. The justifications and impacts of a particular series of measurements can in part be found in the Data Quality Objectives (DQO) document that was prepared and issued to support the particular examinations. As the characterization efforts proceeded these DQOs were not revised to reflect changes in directions dictated by the overall project strategies, schedules, budgets, and technical needs. Changes in planned examinations, to be fully responsive to the overall SNF Project needs, were reflected in the program documentation prepared after the elements were sampled in the basins and shipped to the hot cells for examinations. These documents included examination strategies, test plans, sample analysis plans, letters of instruction, and statements of work, that governed the examinations. The examinations conducted were an integral part of the overall planning and budget process with the Department of Energy for the SNF Project multi-year plans.

Reports of some of the measurements summarized in this report were only documented in Pacific Northwest National Laboratory (PNNL) Highlight Reports, which are not released documents. These specific reports discussed in this summary of the fuel characterization results are included as appendices. A bibliography of additional reports that provide supplementary support to the fuel characterization efforts is also included for completeness.

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2.0 FOCUS AND LIMITATIONS OF FUEL CHARACTERIZATION

The SNF characterization efforts focused on the following two questions:

1. What is the condition of the fuel elements stored in the two basins?
2. How do the fuel elements behave under the process conditions.

A plan was prepared for the characterization of the fuel in the K Basins which addressed these questions but was constrained by the overall schedule for the SNF Project (Lawrence 1995a). Schedule and budget constraints dictated an attribute driven sampling to provide bounding behavior rather than a statistically based characterization program. Fuel examinations are based on two fuel sample selection and shipping campaigns for the K West Basin and one for the K East Basin.

The fuel characterization program was limited to in-situ and laboratory examinations. The Pacific Northwest National Laboratory had overall technical responsibility for a major portion of the laboratory examinations (Lawrence 1998a). Areas of greatest focus for the laboratory examinations were drying characteristics and oxidation kinetics and the degree of combustibility and pyrophoricity.

Some of the reference documents providing the data used in this document are not in full compliance with the quality assurance requirements of the Office of Civilian Radioactive Waste Management (OCRWM) as provided in the Characterization Program Management Plan (Lawrence 1998a). Peer reviews and data validation against the applicable DQOs have not in all cases been performed. Thus, the data and results provided herein must be used with caution.

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3.0 FUEL SAMPLING

An overall strategy was developed for the sampling of the fuel in the two K Basins (Abrefah 1995a). To accomplish the fuel sampling objectives a phased approach was selected. The first phase identified the canisters for sampling. The second phase involved examining these selected canisters and removing specific elements for further visual examinations and possible selection for shipment to the laboratory for detailed examinations. A Data Quality Objectives (DQO) strategy was selected to govern the fuel characterization (Lawrence 1994). A DQO document addresses the following major questions:

- What are the specific SNF Project issues being examined?
- What SNF Project decision (or decisions) must be made?
- What characterization data is required to support the SNF Project decisions?
- How will the characterization data be used to support the decisions?
- How will the characterization data be collected, sampled, and analyzed, and what engineering and statistical methods will be used to evaluate the data?

3.1 DATA QUALITY OBJECTIVES FOR FUEL SAMPLING

The results of the DQO process will be summarized in the following sections covering the two fuel sampling campaigns in K West and the one sampling campaign in the K East Basin.

3.1.1 First K West Sampling Campaign

The first fuel removed from the Hanford K Basins for characterization came from the K West Basin. This initial fuel examination provided unique data on the condition of the fuel in the closed canisters as well as the fuel's behavior in the air atmosphere hot cells during routine handling and examinations (Lawrence 1995b).

The major question to answer was what are the conditions of the materials in the closed canisters? The data to be gathered during the canister opening, handling, transport, associated hot cell handling, and examinations would also support decisions related to the Path Forward primarily in areas of transportation and the Multi-Canister Overpack (MCO) design. In the areas of shipping and transportation the following questions were raised.

1. Will the MCOs be shipped full of water or will the water be drained?
2. What will the gas inventory be during shipping?
3. Will the shipment be in vented or sealed MCOs?
4. Will the shipment be in a horizontal or vertical position?

The examinations to answer these questions are essentially the same as those for the K West fuel with the exception of canister gas and liquid sampling. The focus was the differences in behavior between elements stored in the open canisters in K East compared to the fuel elements stored in the closed canisters in K West.

3.1.3 Second K West Sampling Campaign

The examinations of the second group of K West elements expanded the initial understanding obtained for the fuel stored in closed canisters with emphasis on fuel drying and oxidation behavior (Lawrence 1997a).

The following general questions for the K West fuel relate to the successful design of the fuel processing system and to general project decisions.

- How long does it take to dry damaged K West elements under the Cold Vacuum Drying (CVD) and Hot Vacuum Drying (HVD) conditions?
- How much water remains in the fuel element after drying that may be released to react with the fuel under storage conditions?
- How much fuel degradation will be expected during drying and conditioning?
- How much hydrogen, that must be accommodated by the process equipment, will be released from the fuel elements during the drying process?

In addition to the general questions listed above, data obtained from these examinations addressed the following specific questions. These may not be fully resolved with the data obtained in this sampling campaign.

- What are the locations and morphologies of cracks and are they similar to those in K East? The size of cracks greatly influences the rate at which drying occurs for the underlying material.
- How do the K West damaged elements behave (dripping sludge, widening cracks, etc.)?
- Are the drying and conditioning behavior of the K West elements similar to the K East degraded elements (Lawrence 1996b)? If not, do these differences suggest changes in the fuel processing design?
- Are the K West Basin fuel properties such as oxidation rate, ignition temperatures, and hydride decomposition behavior different from the initial elements from K West or from the K East elements (Lawrence 1996b)?
- What is the internal void volume, amount of trapped sludge, and amounts of water trapped on the exterior and interior of the elements to be removed during drying?

Coatings on fuel elements in K West canisters can be different in texture and color than that on K East elements. Ultimately, a decision needed to be made as to whether: (1) the coatings will be removed mechanically during fuel handling, (2) any water which may be in the coatings will be removed thermally during drying, or (3) the impact of the water will simply be accepted within the current design and safety basis. To support such decisions, the following questions need to be answered:

- To what extent are the coatings adherent and can they be easily removed?
- What is the bound and hydrated water content in the coatings and is it sufficient to suggest that removal of the coating is warranted prior to loading fuel in an MCO?
- Is the adherent K West sludge similar in quantity, adherence, and composition (including hydrates) to corresponding sludge on K East elements?

Examinations to address these questions were very similar to those conducted for the first shipment of fuel from K West. These included video during all in-basin activities, gas and liquid sampling the closed canisters, visual inspection of the element surfaces, hydrogen measurements before fuel shipment, video during hot cell examinations, metallography, whole element furnace testing, TGA, and examination of surface coatings and subsurface sludge.

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4.0 FUEL EXAMINATIONS

The first step in the fuel examinations was a series of in-situ examinations to establish the conditions of the fuel elements in the two basins. These in-situ examinations provided the basis for selection of elements for detailed laboratory examinations as well as provided basin wide damage distributions. These specific examinations will be discussed in the following sections. The elements selected for shipment to the laboratory will also be described and the subsequent laboratory examinations summarized.

4.1 IN-SITU EXAMINATIONS

In-situ examinations included video surveys for fuel damage, gas and liquid sampling the closed canisters, video coverage of all fuel handling and shipping activities, and selected examinations to evaluate fuel element coating behavior.

4.1.1 Video Survey of K East Fuel

The first video survey was a complete examination of all the visible element tops in K East (Pitner 1995). This was later supplemented with full length visual examinations of selected elements. The top only visual examinations were initially to be supplemented by boroscopic examinations to extend the examinations beyond the fuel element tops (Lawrence 1995a). These planned boroscopic examinations were replaced by a "lift and look" examination, recorded on video tape, of 250 elements from 20 preselected canisters (Pitner 1997b).

4.1.2 Gas and Liquid Sampling K West Closed Canisters

The closed canisters in K West were first sampled for gas and liquids to provide initial data on the condition of the elements prior to opening for fuel visual examinations and sample selection (Makenas 1995c). Gas and liquid sampling preceded both fuel sampling campaigns in the K West Basin.

Ten closed canisters were identified for sampling which when examined would satisfy the DQO for the first fuel shipment (Makenas 1995a). They were chosen as meeting criteria such as containing relatively long fuel elements, locking bar integrity, and the availability of gas/liquid interface measurements for associated canister gas traps.

The observations during the first K West fuel shipping campaign were documented in relationship to the sampling strategy (Makenas 1995b). The overall conclusions from the observations of the fuel during the first sampling campaign in K West were that the canisters do contain failed fuel and catastrophic deterioration of the fuel even when failed is not inevitable as was considered a possibility. Removal of this fuel was possible, even when failed, with the proper tools.

The gas and liquid sampling for the second fuel campaign in K West was expanded to 50 closed canisters (Makenas 1996b). These measurements again provided the basis for selection of canisters to open for visual examination and sample selection.

The gas and liquid sampling provided unique data on the contents of the closed canisters to support the design of water cleanup and treatment systems including particle loading in the filters. The closed canisters will be opened for fuel removal and MCO loading and, in order to maintain basin water qualities, the system must be able to accommodate the material sealed in the canisters.

4.1.3 Visual Examinations of K West Fuel

The visual examinations associated with the first fuel shipment were limited to the elements removed for shipment to the hot cells for laboratory examinations. The visual examinations associated with the second fuel sampling campaign included the elements shipped but were expanded to include 250 elements from 20 closed canisters. Each element was removed from the canister, visually examined and then returned to its original storage location. This "lift and look" survey became the basis for the selection of elements for shipment to the hot cells for examination.

4.1.4 Other In-Situ Examinations

All fuel handling, selection, and shipping activities in the basins were recorded on video tape (in some cases using multiple cameras with different perspectives). These data, in addition to documenting what was done, provided information on canister and fuel element behavior during routine handling in the basins. Supplemental data were obtained from similar video records of critical fuel movements, handling, and examinations in the air atmosphere hot cells.

Visual examinations of the elements in K East and K West showed the presence of surface coatings on the elements. These coatings were different for the two basins. Examinations of these surface coatings in the Basins included measurements of surface coating thicknesses on K West elements using nondestructive techniques (Pitner 1998b). Coating adherence tests were conducted on selected elements using brushing techniques as well as simple rocking tests to simulate possible element motion during element cleaning (Bergmann 1996).

4.2 ELEMENTS SELECTED FOR LABORATORY EXAMINATIONS

4.2.1 First K West Sampling Campaign

The first fuel removed from the Hanford K Basins for characterization came from the K West Basin. This initial fuel examination provided unique data on the condition of the fuel in the closed canisters as well as the

fuel's behavior in the air atmosphere hot cells during routine handling and examinations (Lawrence 1995b). A total of three elements were selected for laboratory examinations. The three elements selected were:

- A broken Mark IV fuel element: Characterization of this sample showed the degree of degradation of K West fuel, with exposed uranium metal, within the closed K West canisters, and whether stabilized uranium hydride has formed in this environment. This addressed assertions that the K West fuel is more degraded and/or pyrophoric than the K East fuel.
- A slightly breached Mark IV fuel element with length codes S or E: Characterization of this sample allowed evaluation of the effects of limited water access to the area of corrosion and possible enhanced uranium hydride formation.
- A visually intact fuel element: Characterization of this sample indicated whether the encapsulation of intact N Reactor SNF elements in K West adequately protected it from long-term degradation. The visibly intact fuel elements may contain incipient failure sites most likely in the areas of the braze that seals the end cap on the elements.

4.2.2 K East Sampling Campaign

One fuel sampling campaign was conducted in the K East Basin with open canisters. The scope of these examinations of the K East fuel focused on the initial behavior of the fuel stored in open canisters during fuel movements, the extent of fuel degradation, the fuel's response to drying, and the degraded fuel's pyrophoric behavior (Lawrence 1996a). A total of nine elements were identified for selection for the detailed laboratory examinations. Fuel element visual appearance was identified as the major factor in fuel selection. The K East video survey was the primary source of information for selection of the canisters to examine for possible element selection (Pitner 1995).

A total of 64 canisters were selected for the screening examinations from which to narrow the candidates for canisters to sample for the required nine elements (Makenas 1996a). The 64 were chosen according to the following criteria.

- Canisters must have the potential to satisfy the DQO identified needs. These include damaged fuel, the need for replicates of the same damage level, bubbles indicating ongoing corrosion, and/or corrosion sufficient to indicate potential sludge.
- Canisters must be under basin grating slots for ease of canister handling due to equipment availability at the KE Basin.
- The list must be of a size to be surveyed in 2 weeks. Sixty-four was judged to be an achievable number based on experience during the 1994 video campaign (Pitner 1995).

- The list must include some older fuel as defined by the data base of key dates and encapsulation dates.
- Aluminum canisters, with potential for canister corrosion product in the sludge, must be included.
- At least some of the candidate damaged elements within the suggested canisters must be easily handled with existing tools unless the canister is a candidate only to supply sludge samples.
- Candidate canisters must not be near stacks of debris and empty canisters which might take inordinate time to move and which might interfere with survey or canister handling equipment.
- Candidate canisters with badly split fuel elements (with potential to damage survey equipment) may be included but must be surveyed last to avoid jeopardizing completion of the bulk of the survey.

4.2.3 Second K West Sampling Campaign

Examinations for the second group of elements from K West expanded the understanding obtained from the initial sampling of elements stored in the closed canisters. Elements were selected for examination with emphasis on supporting whole element furnace testing and TGA measurements for oxidation behavior, drying, and hydrogen release (Lawrence 1997a). The DQO called for a total of 15 elements with 11 dedicated to whole element furnace testing. The actual division of elements for testing was to be based on the condition of the elements selected and transferred to the hot cells. Twenty canisters were identified for sampling to remove the 15 elements to meet the requirements of the DQO (Makenas 1997a). The actual condition of the 15 elements shipped to the hot cells was established from the video records during sample selection.

4.3 LABORATORY EXAMINATIONS

Selected elements were sent to the hot cell for laboratory examinations. Examinations of the elements included determining the physical condition with detailed visual examinations and selective destructive examinations to characterize surface coatings and accumulations of subsurface sludge. Small samples were removed from selected elements for total hydrogen content and metallography for oxide layer and hydride characterization. Controlled atmosphere furnace tests were conducted with small samples for fuel behavior during drying and conditioning and as a precursor for whole element drying tests. Oxidation rates were measured in different atmospheres with the small samples using Thermo-Gravimetric Analysis (TGA). Whole elements were dried in a controlled atmosphere furnace to determine behavior under cold vacuum drying (CVD) conditions and to establish the water content following CVD.

4.3.1 Laboratory Examinations of K West Elements

An examination strategy was developed for the 15 elements based on their visual appearance. The examination strategy identified the first group of elements for whole element furnace testing, for characterization of surface coatings and subsurface sludge, and to provide small sample for TGA testing for oxidation rate measurements (Lawrence 1997b). Five damaged elements were selected for the first phase of whole element furnace testing with three elements selected for coating and subsurface sludge examinations.

A similar strategy was developed for the Phase II whole element furnace testing (Lawrence 1998b). The remaining seven K West elements were identified for additional fuel drying tests, oxidation tests in the whole element furnace, and drying elements for post CVD staging tests. The Phase III whole element furnace testing was to focus on the K East damaged fuel elements.

4.3.2 Laboratory Examinations of K East Elements

The K East elements shipped to the hot cells were nondestructively examined and a strategy developed based on their condition for the planned examinations (Pitner 1997a; Lawrence 1996b). The strategy, based on the visual appearance, identified three elements for surface coating and internal sludge examinations and six elements for whole element furnace testing. Two of the elements for surface coatings and internal sludge examinations were also identified for sectioning to provide small samples for TGA testing, metallography and possible tests in the small furnace.

A strategy was developed for TGA of the K East fuel samples (Lawrence 1997c). Tests were first to establish if there were any differences for dry air oxidation between the K East and K West fuel. Those tests were to be followed by moist-inert oxidation measurements, evaluation of the possible element to element behavior, and oxidation in steam.

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5.0 RESULTS OF FUEL EXAMINATIONS

The characterization activities completed for the K West and K East fuel elements are summarized in Figures 1 and 2 in relationship to the two questions which were the focus of the examinations.

The extent of the various fuel examinations summarized in Figures 1 and 2 do not fully support the original objectives of the DQOs and examination strategies. Changes in the SNF Project direction resulted in changes in the process strategy and the corresponding technical questions to be addressed by the fuel characterization. These numerous changes in Project priorities dictated revisions to the on-going characterization activities to be fully responsive to the most pressing technical questions.

These changes in the characterization activities were reflected in the integrated multi-year activity plan (MYAP) for the overall SNF Project. The MYAP governed what characterization activities were conducted to be fully responsive to the SNF Project goals. Budget and schedule constraints also entered into the revision to the fuel characterization plans again reflected in the overall MYAP for the Project.

The overall logic and justification for these changes are beyond the scope and objectives of this document. The justification for the changes in the direction of fuel characterization is contained within the documentation supporting the MYAP.

The results of these examinations will be summarized in the following sections covering extent of fuel damage, physical condition of the elements, behavior during handling, properties, and response to process conditions.

The results of the examinations of the first three elements from K West were documented in two detailed data reports (Abrefah 1995b, 1996). Subsequent examination data were reported in reports covering specific topics including the unpublished Highlight Reports included in Appendices A and B of this document.

5.1 EXTENT OF FUEL DAMAGE IN BASINS

The gas and liquid sampling of the K West closed canisters preceded and formed the basis for selection of canisters to be opened for visual examinations and sample selection. The initial sampling campaigns provided data to support the assessment of risks associated with opening the canisters in the K West Basin as well as valuable correlations of closed canister chemistry with the observed fuel condition upon opening the canisters. Gas generation in the closed canisters was of particular interest.

The gas and liquid sampling also provided valuable data applicable to water cleanup and air permits associated with opening the canisters of fuel in the K West Basin.

Figure 1. Summary of K West Basin Spent Nuclear Fuel Characterization.

1. What is the condition of the fuel elements?

RG98100263.2

Figure 2. Summary of K East Basin Spent Nuclear Fuel Characterization.

1. What is the condition of the fuel elements?

2. How do the fuel element behave under process conditions?

RG98100263.1

Results of the gas and liquid sampling will be discussed only in their relationship to fuel conditions. Specific results of the two sampling campaigns can be found in Trimble (1995a, 1995b, 1996, 1997a, 1997b).

The results of the visual survey of K East Basin (Pitner 1995) and the K East full length visual examinations (Pitner 1997b) and the corresponding K West fuel visual examinations (Pitner 1997c) were collected in a summary assessment of the fuel damage in the K Basins (Pitner 1998a).

Fuel conditions in these assessments were rated based on the following four categories.

- Intact - No evidence of cladding breach or deposited sludge.
- Breached - Minor cladding rupture with no reacted fuel or deposited sludge visibly present.
- Defected - Definite evidence of cladding breach with reacted fuel egressing from the element. The amount of exposed fuel may be significant, but there is no gross cladding splitting, element dilation, or fuel voiding.
- Bad - Gross failure is evident with substantial element dilation, cladding splitting, fuel "mushrooming," or fuel voiding.

The resulting damage distributions for fuel elements in the two basins are given in Table 1. Fuel elements in the "Bad" category can be considered scrap basket candidates, while the remaining fuel for the most part should be loadable into fuel baskets.

Table 1. Fuel Damage Distributions.

Fuel Condition Category	K East		K West	
	Inners (%)	Outers (%)	Inners (%)	Outers (%)
Intact	86	49	84	50
Breached	9	9	14	39
Defected	4	38	0	0
Bad	1	4	2	11

The majority of the damage occurs in the outer elements, which is to be expected based on their greater vulnerability during discharge and handling operations. About 85% of the inner elements and about half of the outer elements in both basins are considered to be "Intact." It is seen that there are no K West fuel elements in the "Defected" category. This presumably reflects the effectiveness of the corrosion inhibitor added to the canisters.

The relative portion of "Bad" outer elements in K West is notably greater than for K East in Table 1 (11% versus 4%). This is probably at least partially due to the nature of the canisters examined in the surveys. The K East results are based on a full basin survey, while the K West canisters examined were a selected few chosen with the objective of locating damaged fuel for laboratory examinations. Most of the K West canisters examined had high cesium level readings in liquid samples previously taken from the canisters, presumably an indication of failed fuel contents. Thus, it might be expected that the K West results would be biased toward a higher damage state.

It should also be pointed out that while the fraction of "Bad" elements is greater for K West, the actual degree of damage on "Bad" K West elements is generally less than observed on "Bad" K East elements (Pitner 1998a).

A statistical analysis (Welsh 1998) was recently performed of the K West visual examination results in an attempt to correlate fuel damage with various storage conditions (canister type, fuel type, key date, years since encapsulation, ^{240}Pu content) and measured parameters (gas trap readings, ^{137}Cs concentration, potassium concentration, fuel coating, and qualitative sludge level). No statistically significant correlations were identified in this effort, and the damage distributions basically remained the same as presented in Table 1.

The gas and liquid sampling data from the 50 canisters (100 barrels) were used to provide an estimate of badly damaged fuel for the larger population of K West closed canisters using the visual examinations data and the corresponding ^{137}Cs measurements for the canister barrels (Trimble 1998). A correlation between the number of "Bad" fuel elements in a canister barrel and the ^{137}Cs data was found. This correlation and the assumed distribution of ^{137}Cs for all K West Basin barrels was used to estimate the overall fraction of "Bad" fuel in K West Basin. The resulting estimate, 10.7% with an uncertainty of about $\pm 4\%$, is consistent with the 11% value from the visual examinations only (Table 1).

5.2 PHYSICAL CONDITION OF ELEMENTS

The physical condition of the elements was established with both in-situ and laboratory examinations. The specific areas addressed for the physical condition of the elements in the K Basins were surface coatings, subsurface sludge, exposed fuel oxide layers, fuel hydride content, and fuel to cladding bond integrity. Subsurface sludge was of interest since this material is expected to accompany the fuel elements in the MCO. The results of these examinations will be summarized in the following sections of this report.

5.2.1 Surface Coatings

Surface coating material was removed from four K West and one K East fuel elements for examination (Pitner 1997d). A strategy was developed for the examinations of these fairly small volumes of recovered material (Makenas 1997b).

The coating on the K East elements recovered can be characterized as a light grey material of a relatively uniform thickness. The coatings observed on the K West elements included a relatively thick translucent white colored coating, a dark gray coating, and a bright orange coating.

During a separate campaign the gray coating on the K East elements was removed from two additional elements during hot cell examinations. This material was determined to be predominately uranium based compounds (Abrefah 1998a). The character of the coating material suggests the coatings may be formed as part of a nucleation and precipitation process.

The coatings on the K West elements have been determined to be primarily iron based compounds when the relatively thick translucent white coating is not present. This translucent white colored coating has been determined to be $\text{Al}(\text{OH})_3$ (Makenas 1998a). Scanning electron microscopy examinations of the aluminum hydroxide coatings removed show a coating thickness of approximately 40 μm to 60 μm .

The extent, thickness, and behavior of some of these coatings were established with three different examination activities in-situ. Coating adherence was established with an initial series of in-basin examinations where elements were subjected to brushing and, in one case, controlled rolling to remove the coating. The latter test, in the K East Basin, included two inner and one outer elements (Bergmann 1996). Minimal amounts of coating were removed where one element rubbed against another element on the container. Brushing of K East elements was found to remove the surface coatings.

Subsequent testing included fuel elements from K West with the different appearing coatings brushed to determine the adhesiveness of the coatings (Maassen 1997). A total of eight elements were tested. The gray coatings were relatively easily removed. The orange rust-like coating results suggest stronger adhesive to the surface but the coating was removed with moderate efforts. The aluminum hydroxide coating was not easily removed with the steel brushes under water. The most recent coating examinations in K West included a series of brushing tests using different brush types which proved very effective in removing the aluminum hydroxide coating (Pitner 1998b). In these tests, with a motorized brush, the thickest aluminum hydroxide coatings were removed in approximately 1 minute.

Finally, aluminum hydroxide coating thicknesses were measured on 37 outer elements and eight inner elements in the K West Basin using eddy current techniques (Pitner 1998b). Measured coating thicknesses ranged from 0 μm to 150 μm . Coatings measured on the inner elements of fuel assemblies that protruded into the cover gas space above the water in the closed canisters were notably thinner than those found on corresponding outer elements. Limited data also suggest a dependence of coating formation on the pH level of the canister water. A higher pH promotes coating formations.

5.2.2 Subsurface Sludge

Two outer elements from the K West Basin and one outer element from the K East Basin were destructively examined to quantify and determine the

composition of the sludge trapped within the elements (Pitner 1997d). This material may be expected to accompany the fuel in the MCOs. The void and crack depths of the breached elements were measured with a calibrated probe. The loose cladding around damaged areas on the fuel elements was peeled away exposing the damaged fuel. After peeling, the exposed fuel was worked, primarily with a pick tool, to recover as much particulate material as possible.

The open area of the center breach areas of two elements was estimated using the calibrated probe. Both elements with center breaches were from the K West Basin. The particulate samples obtained were weighed after several hours of drying time, so the values should basically represent particulate mass quantities after evaporation of the free water. The derived particulate concentration per unit area of initial crack opening is listed in Table 2.

Table 2. Subsurface Particulates for Breached K West Fuel Elements.

Element/ Breach Location	Particulate Mass (g)	Breach Area (cm ²)	Particulate Concentration (g/cm ²)
6743U/Center	4.42	2.39	1.85
7913U/Center	8.19	3.96	2.07

The average of these two measured particulate concentrations is 1.96 g/cm², with a standard deviation of 0.16 g/cm². While as much particulate material as possible was recovered from the damage areas, it probably was not complete. Considering that sample recovery was less than complete, and the uncertainty involved in estimating the open breach areas, a conservative value for the particulate concentration beneath open breaches might be 3 ± 1 g/cm². Chemical analysis shows the particulate to be primarily uranium (Makenas 1998b). If this particulate material is uranium oxide with a density of about 10 g/cm³, then the volumetric concentration of particulate material beneath open breaches would be 0.3 cm³/cm². This corresponds to a particulate depth of 0.3 cm beneath open breaches, if the fuel corrosion did not extend laterally beneath the open breach area.

5.2.3 Fuel Oxide Layers

The thickness and character of the oxide layers formed on the corroded fuel were determined from metallography of selected samples of a K West breached element (Marschman 1997). Eight samples were examined from the element mid-length and damaged end. Some of the samples had been subjected to controlled oxidation in Argon-2% oxygen atmospheres at 250 °C for 10 hours.

Portions of a very thin oxide layer were observed along the fuel edges of most specimens. The layer appeared to be porous and was obviously non-adherent. Typically, it had pulled away from the fuel and appeared to be flaking off. In all but one case, the maximum thickness of the layer was 3 μm. The one exception was a very short fragment about 10 μm thick on a specimen that was subjected to the controlled oxidation.

5.2.4 Fuel Hydride Content

The presence of uranium hydrides, i.e., UH_3 , was verified with metallography and hydride contents were quantified with total hydrogen release measurements for both the small sample tests in the TGA and whole elements subjected to high temperature drying conditions.

Uranium hydride inclusions were observed in each metallographic sample examined (Marschman 1997). The most extensive hydride was seen in the sample from the damaged end of the element, as expected. The largest hydride inclusion seen measured approximately 250 μm in diameter. This sample from the damaged end of the element showed an extensive network of macro-cracks. The large hydride inclusions were more prevalent in this region of the sample. Smaller hydrides were distributed throughout the sample but appear more prevalent near the larger inclusion and the macro-cracks.

Six small samples from the damaged regions of two K West elements were subjected to high temperatures under vacuum conditions in the TGA to measure total hydrogen release. The highlight report covering these measurements is included as Appendix A to this report. Hydrogen released was converted to the quantity of uranium hydride present in the sample. Hydrogen concentrations ranged from 18 parts per million by weight (wppm) to 80 wppm. This highest concentration converts to approximately 1 volume percent uranium hydride in the samples assuming the theoretical density for uranium hydride. This is considered to be a lower bound due to various limitation of the measurements. The decomposition reaction for the hydrides started at a temperature above 100 $^{\circ}\text{C}$ and essentially all the hydrogen was released by 400 $^{\circ}\text{C}$.

Hydride contents of whole damaged elements were similarly determined from total hydrogen release in the whole element furnace. Six damaged K West fuel elements were subjected to both CVD and high temperature drying to determine drying behavior (Lawrence 1998c). Significant quantities of hydrogen were released from the whole damaged K West elements due to oxidation of fuel by available water and decomposition of uranium hydrides at the higher temperature. The largest contribution to the hydrogen released was from the uranium hydrides. The individual hydrogen peaks were deconvoluted and the quantity of hydrogen released from the hydride estimated. This quantity of hydrogen was converted to the amount of UH_3 that was decomposed. The amount of UH_3 decomposed ranged from 0.5 g for the least damaged element to 40 g from the element with extensive axial cracking. Hydride content was the highest in the element with no end breaches and extensive axial cracking. This appears consistent with metallographic examinations which suggested the hydrides were concentrated in fuel cracks ahead of the oxidized fuel interface. The narrow axial cracks appear to have enhanced hydride formation with minimal fuel oxidation.

5.2.5 Fuel Cladding Bond

Metallography showed the fuel-to-cladding bond to be intact along its full length in each of the samples. Uranium hydride inclusions, uranium carbide inclusions, and local areas of fuel pull out (shallow pits) were observed immediately adjacent to the bond on several specimens at a number

of locations (Marschman 1997). However, the integrity of the bond did not appear to be affected. No stringers or extensive void networks were found along the exposed length of the bond region, indicating the fuel-to-cladding interface did not serve as a preferential path for the migration of hydrogen or the ingress of corrosion.

5.3 FUEL BEHAVIOR DURING HANDLING FOR SAMPLING AND EXAMINATIONS

A small degree of breakage was experienced during in-basin handling of fuel elements. However, as a rule the fuel appeared to be quite robust in nature and retained generally good physical integrity during the varied handling operations (Pitner 1998c).

Fuel handling and examinations in the laboratory were conducted in air atmosphere hot cells. There were no incidents, during the fuel handling in the hot cells, of rapid fuel oxidation or degradation as a result of the exposure to air at ambient temperatures. Elements were also sectioned in the air cells, but a flowing inert cover gas was utilized for sample protection.

Several instances of sparking were noted during the destructive examinations for subsurface sludge when the cladding was peeled away from the damaged areas of three elements (Pitner 1997d). It was estimated that a sparking event occurred about a third of the time that cladding strips were pulled from the elements. The sparks are believed to be generated by small particles of freshly exposed cladding break off, are ejected, and burn as the strip is peeled free. Fine zirconium particles below approximately 10 μm , as well as uranium metal, are known to ignite spontaneously when dispersed in air at room temperature (Metals Handbook 1961).

Observations of fuel behavior were made during the fuel coating and subsurface sludge examinations in the hot cells (Pitner 1997d). Despite the fragile physical appearance of some of the fuel elements examined, they actually proved to retain substantial structural integrity. Considerable effort was required to physically break the elements or break fuel pieces free from the elements. While the cladding probably lost some ductility during irradiation, it could not be generally classified as brittle. Repeated flexing of the cladding strips was typically required to break them loose. They generally broke at a point where the fuel remained bonded to the cladding.

5.4 FUEL PROPERTIES FOR PROCESS AND SAFETY

The two fuel properties with the greatest impacts on process and safety analysis for the SNF Project are fuel ignition and oxidation. Results of the measurements to determine these two basic material properties for the irradiated and degraded N Reactor fuel material are summarized in the following sections.

5.4.1 Fuel Ignition

Seventeen ignition tests were performed in dry air on samples removed from two K West damaged fuel elements (Abrefah 1998b). One of the elements was breached with extensive corroded fuel whereas the other element was nearly completely sheared off on one end and is referred to as sheared fuel. Selected samples were either left in their unaltered state or subjected to controlled oxidation conditions, i.e., conditioning, prior to ignition testing to evaluate the relative improvements in pyrophoric behavior for conditioned fuel. Conditioned samples were dried for 10 hours at 50 °C under vacuum condition and for 24 hours at 300 °C. Samples were then exposed to 2% oxygen in argon at one atmosphere pressure at 250 °C for 11 hours.

Results of ignition tests on specimens sectioned from the corroded end of the K West SNF showed that the potential for ignition is high. The corroded specimens had consistently lower ignition temperatures (regardless whether conditioned or not) than the mid-section specimens which were distant from the corroded regions of the fuel element. An ignition temperature below 300 °C was measured for as-cut corroded samples. Overall, the ignition temperatures of these samples were in the temperature range of 277 °C to 500 °C whereas, ignition temperature of the samples from the mid-section of the element was about 650 °C. These tests confirm that small pieces of corroded fuel with a large specific area can ignite at a temperature lower than the expected literature ignition temperature for metallic uranium.

Dried and conditioned samples from the corroded fuel with similar pre-test conditions were tested and found to ignite at temperatures higher than as-cut sibling samples. However, the same tests performed on the sheared fuel did not yield favorable results. Differences in reactive surface areas and the possible inability of conditioning to decompose hydrides in occluded areas in the sheared fuel may be the reasons for the different response. The tests were conducted with some uncertainties concerning the initial specimen conditions.

5.4.2 Fuel Oxidations

Fuel oxidation measurements were conducted using two separate independent experimental systems. A tube furnace was used to measure the oxygen uptake of samples in flowing 2% oxygen 98% argon atmospheres. A TGA system was used for a series of dry air, moist air and moist-inert oxidation measurements (Abrefah 1998c, 1998d).

Results of the tube furnace tests show differences in the oxidation rate of samples taken from the damaged/corroded and undamaged regions of the same K West element (Abrefah 1998c). Samples taken from the damaged/corroded regions of the element showed an oxygen pickup rate that was time independent, indicating a linear oxidation behavior. However, the oxygen pickup by the samples taken from the undamaged regions decreased with increasing time that suggests a protective oxide film formation on the samples.

The average oxidation rate for the undamaged fuel samples in an oxygen/argon atmosphere at 250 °C was 7.01×10^{-3} mg/cm²/min. This rate is in close agreement with the value 4.16×10^{-3} mg/cm²/min estimated from unirradiated literature data. On the other hand, the average oxidation rate of the damaged fuel samples at 250 °C was 2.15×10^{-2} mg/cm²/min, which is about a factor of five greater than the unirradiated uranium data. In one particular experiment, the oxidation rate of damaged fuel samples at 150 °C was 1.24×10^{-2} mg/cm²/min, which is about 83 times greater than estimated from the literature. This sample showed significantly higher hydrogen release during its drying step compared to other samples. Thus, the increased oxidation rate observed for this sample may be due to an enhancement effect of uranium hydride inclusions in the sample.

The data for dry air oxidation of damaged/corroded fuel samples using the TGA showed an oxidation behavior that was complex (Abrefah 1998c). The data were grouped into two categories for analysis. The first group of data represents the cases when the weight change by the sample followed a typical metallic material oxidation kinetics. The second group of weight change showed oxidation behavior that was very erratic due to effects that include but are not limited to (1) sample cracking, (2) rapid oxidation of the sample resulting in large volume changes, (3) spallation of the oxide film, and (4) disintegration of the sample due to rapid oxidation of particulates, perhaps hydrides, in the matrix. The shape of the weight change data for the first group could be fitted with either linear or parabolic oxidation kinetics (Abrefah 1998c).

Five fuel samples from a damaged element from K West Basin were oxidized in the TGA in flowing air containing moisture. The partial pressure of the moisture in the gas stream was the same (i.e., 12.33 kPa) for all five tests, but the isothermal condition was varied between 198 °C and 350 °C. The SNF oxidation behavior in moist air at a temperature of 198 °C can best be fitted by parabolic oxidation kinetics (Abrefah 1998d). A linear rate equation gave the best fit to the oxidation data at 250 °C and above. The results within the temperature range studied, therefore, show a transition from parabolic oxidation kinetics (i.e., protective oxide layer) to linear oxidation kinetics (i.e., cracking and spallation of the oxide layer). The transition temperature is somewhere between 198 °C and 250 °C.

The tests at approximately 300 °C gave results that were very different from the other tests at temperatures of 198 °C, 250 °C, and 349 °C. The weight change at this temperature showed erratic behavior. Visual examination indicated the sample fragmented into small pieces and powder as a result of rapid oxidation and hydration. There was no significant difference between the moist air oxidation rate and the dry air oxidation rate of sibling samples within this temperature range. This result is consistent with expectations based on the limited literature values for the effects of moisture on oxidation rates for irradiated uranium.

TGA measurements of K West damaged fuel oxidation in moist inert atmospheres at temperatures of 150 °C or lower are currently in progress at PNNL. These results will be reported separately in a PNNL document and are not summarized in this report.

5.5 FUEL RESPONSE TO PROCESS CONDITIONS

Fuel element response to the process conditions for drying were established with small sample testing in the tube furnace and later expanded to whole element tests.

The description of the small sample furnace and the result of the corresponding tests for fuel drying and for proposed conditioning were reported in PNNL Highlight Reports which are included as Appendix B to this report. The result of these tests provided the basis for extending the testing to whole damaged K West fuel elements. The specific results of these small sample tests are not summarized here but can be found in Appendix B. The whole element furnace test results summarized in the next section provide the basis for the drying process behavior.

5.5.1 Whole Element Furnace Tests

One K East and seven K West elements were subjected to high temperatures and vacuum conditions to remove water (Lawrence 1998c). Six of the K West outer elements had cladding breaches that ranged from a simple fracture at the approximate mid-point to severe damage with cladding breaches at the top and bottom ends including axial breaches and fuel loss. The results of these tests were collected in the summary report which focused on the six tests with breached elements (Lawrence 1998c). The results of each individual test can be found in the PNNL reports listed in Table 3 and listed in Section 6.2.

Table 3. Whole Element Furnace Drying Tests.

Furnace Run Number	Element Number	Element Type	Extent of Fuel Damage	PNNL Report Documenting Test Results ²
1	1990	I	Undamaged	PNNL-11817
2	3128W ³	O	Undamaged	PNNL-11818
3	0309M	O	Broke in half	PNNL-11820
4	5744U	O	Top breach and axial cracks	PNNL-11821
5	6603M	O	Bottom breach	PNNL-11841
6	1164M	O	Mid-element cracks	PNNL-11896
7	2660M	O	Severe damage	PNNL-11897
8	6513U	O	Severe damage	PNNL-11969

¹I = Inner, O = Outer element.

²For a complete list of references see Section 6.2.

³A K East element, all other elements are from K West.

Drying under conditions typical of cold vacuum drying (CVD) removed between 10 ml and 30 ml of free water from the six damaged elements. High temperature vacuum drying determined that between 1 g and 3.3 g of water remained in the elements after conditioning typical of CVD. One element with a translucent coating, determined from laboratory examinations of similar appearing coatings to be aluminum hydroxide, released 1.7 g of water from the coating. This amount of moisture is consistent with independent characterizations of similar coating materials. The amount of water remaining after CVD appears to be relatively insensitive to the extent of fuel damage once there has been fuel degradation and cladding opening.

The high temperatures that the elements experienced resulted in changes in the appearance of the surface coatings and the axial fuel cracks. The changes in the appearance of the axial cracks are generally considered to be the result of oxidation of the underlying fuel material with the corresponding volume increases of the less dense oxides.

Measurable quantities of fission product gases, xenon and krypton, were detected with the down stream mass spectrometer in two of the furnace runs. Isotopic percentages of the fission product gases were found to agree closely with calculated values. Fission product gases were released from the fuel as a result of the oxidation of fuel by available oxygen during the high temperature portions of the tests, i.e., 75 °C or higher.

Significant quantities of hydrogen were released from the elements due to oxidation of fuel by available water and decomposition of uranium hydrides at the higher temperature. The largest contribution to the hydrogen released was from the uranium hydrides.

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A P P E N D I X A

**HIGHLIGHT REPORT COVERING HYDROGEN RELEASED FROM
CORRODED/DAMAGED K WEST NUCLEAR FUEL IN VACUUM**

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Highlight Report: Hydrogen Released from Corroded/Damaged K-West Spent Nuclear Fuel in Vacuum

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SNFCT97:032

SUMMARY

A hydrogen release study performed using the TGA/MS system on samples taken from the corroded regions of N Reactor outer elements yielded concentrations above the nominal as-fabricated values. The concentrations measured ranges between 18 wppm to 80 wppm. The highest concentration (i.e., 80 wppm) translates to about 1 v/o of the material in the form of uranium hydride (theoretical density of uranium hydride was assumed for the conversion). These concentrations represent a lower bound due to the following limitations in the measurements.

- 1) A fraction of the hydrogen released by dissociation of the hydride can react with adsorbed oxygen on the sample surface to form water. This fraction could not be discerned from the background water signal in the system.
- 2) At higher temperatures, the reactivity of uranium with moisture in the chamber generated hydrogen which constitutes a large fraction of the hydrogen signal. Because of this, the fraction of hydrogen from hydride at high temperatures were not included in the calculations.
- 3) The small cracking fraction of the decomposed hydrogen to atomic hydrogen signal in the mass spectrometer (MS) was ignored because of the larger source of atomic hydrogen from cracking of water molecules.

The decomposition reaction of hydride in the SNF samples started at temperatures above 100°C and most of the observed hydrogen was released when the sample temperature was about 400°C. The peak hydride decomposition temperature varied from sample to sample, but ranges between 235°C to 332°C.

INTRODUCTION

The Hanford Spent Nuclear Fuel project proposal for moving the irradiated N Reactor fuel from its current storage in the 105-K Basins to interim dry storage involves sealing the SNF in a multicanner overpack (MCO) and storing for a period not less than 40 years. The SNF has been corroding in the storage pools which has generated corrosion products (mainly oxides of uranium and uranium hydride). The presence of hydrides above certain threshold concentrations may influence certain behavior of the SNF during handling and processing. One of these characteristics that have safety consequences is the thermal decomposition of the hydride which can supply hydrogen gas to the MCO during processing or storage. Knowledge of the thermal decomposition behavior of the hydride inclusions in the SNF is needed in calculations that address deflagration mixture of gases in the MCO during storage and during the drying process.

This highlight report discusses results of hydride decomposition studies of SNF fuel samples in vacuum using a thermogravimetric/mass spectrometer (TGA/MS) system that monitors the weight change of the samples due to volatilization of species such as water, thermal decomposition of any hydride phase and oxidation of the core uranium metal. The volatilized species were monitored by the quadrupole mass spectrometer. The tests were conducted to determine the relative amount of hydride in the samples and the temperature ranges where the hydrides can thermally decompose.

EXPERIMENTAL

The schematic of the TGA/MS testing system is shown in Figure 1. A detailed description of the system is in the report of Marschman and Abrefah (1996).

The SNF samples used for the hydrogen release tests were taken from the damaged/corroded regions of SNF elements SFEC5,4378 and SFEC10,4366. The irregular-shaped samples were used in the as-cut condition without any further preparation. They were weighed and limited dimensional measurements were taken for rough size determination. The samples were heated at rate of about 3°C/min to about 700°C in a vacuum (about 10^{-3} Torr). The sample weight change was continuously monitored by the electrobalance throughout the test and the off-gas stream was analyzed by the attached quadrupole mass spectrometer.

After completing all the hydrogen release tests, the MS was calibrated by running a standard gas at a flow rate of 25 cm³/min through the system for a period of time. The standard gas mixture contained 3.6 vol% hydrogen and a balance of helium with impurity levels less than one ppm. The MS signals for hydrogen and helium were analyzed to determine the volume ratio for comparison with the vendor's specification.

The calibrated MS signal for hydrogen was used to calculate the proportionality factor, F (cm³/nA-min), for converting the hydrogen signal to volume of hydrogen at STP. The value for F

was $0.2 \text{ cm}^3/\text{nA}\cdot\text{min}$. and the areas under the hydrogen intensity curves were multiplied by this factor to give volumes of hydrogen.

RESULTS AND DISCUSSION

Results of six TGA runs performed are shown in Figures 2 through 7. All the runs show two characteristic forms of hydrogen (first and second peaks) except the reruns of TGA 27 (Figure 6b) and TGA 28 (Figure 7b). The first release of hydrogen occurred during the initial sample temperature ramp and most of the release happened below 400°C . This first observed hydrogen peak was interpreted to originate from thermal decomposition of uranium hydride inclusions in the sample and later tests were designed to confirm this. The second and large hydrogen peak observed at higher temperatures was attributed to hydrogen generation by reaction of the bulk uranium sample with moisture in the system. However, at higher temperatures, any unreacted uranium hydride inclusions may contribute to the total hydrogen released. The last two TGA runs (TGA 27 and 28) were performed in support of differentiating these two sources of hydrogen observed.

In run 27 (Figure 6a), the sample was heated to a maximum temperature of 400°C compared to 700°C for Figures 2 through 5. The results plotted in Figure 6a show a lower contribution of hydrogen by the reaction process and almost a complete release of hydrogen from the sample by the hydride decomposition process. When this drained sample was reheated with the same temperature profile, the first peak (attributed to hydride decomposition) was not observed (Figure 6b). The small amount of hydrogen generated by the reaction of uranium with moisture in the system was observed. The characteristic shape of the second peak also supports a reaction process because it increases with increasing temperature, remains constant at constant temperature and decreased to the background level when the temperature was decreased to ambient conditions.

Figures 7a and 7b show the results of run 28 which was similar to run 27 except that the maximum temperature was increased to 800°C . Again, only the initial run (Figure 7a) showed the first hydrogen peak ascribed to thermal decomposition of uranium hydride inclusions in the sample. This run showed an increase in the hydrogen release resulting from the reaction of the sample with moisture (second hydrogen peak) in the system. The increased hydrogen signal with increasing temperature for the second temperature cycle (Figure 7b) can be explained by a reaction process. The absence of any hydrogen signal during the repeat cycle for TGA 27 and 28 also indicates that hydrogen generation from reaction at lower temperatures was negligible. Thus, the contribution of hydrogen to the first peak from a reaction of the sample with moisture present in the system at lower temperatures can be ignored.

The first peak of each run was integrated, taking the baseline as the minimum point on the curve, to determine the area under the peak. The area was then multiplied by the calibration factor, F, to determine the volume of hydrogen released. The volume of hydrogen was converted to hydrogen

weight at standard temperature and pressure (STP). The results of these calculations are listed in Table 1. The hydrogen concentrations of the SNF samples ranges between 18 wppm to 80 wppm. The measured concentrations are above values for nominal hydrogen inventory in the as-fabricated N Reactor fuel. Typical concentration quoted for as-fabricated N Reactor material is 2 wppm. (Smith 1989). The increase in hydrogen concentration observed for these samples can be ascribed to two sources; (a) during reactor operation where hydrogen generated by various oxidation reactions of the water coolant with the fuel and other reactor components found its way into the fuel matrix, and (b) during K Basin storage where a fraction of the hydrogen generated by the fuel corrosion dissolved in the fuel. The latter is considered the major source during since in-reactor operation most of the hydrogen generated will thermodynamically dissolve in the Zircaloy cladding material unless there was a breach in the cladding.

Due to the low solubility of hydrogen in uranium (Mueller 1968) most of the hydrogen measured in the sample matrix was in the form of uranium hydride phase. The weight fraction of hydrogen in a pure uranium hydride phase is 1.24×10^{-2} . Using this number and assuming maximum theoretical density for the hydride inclusions, the maximum hydrogen concentration (80 wppm) translates to 1.2 v/o of the sample is uranium hydride.

The hydrogen signal for each first peak started at temperatures above 100°C and showed a maximum. The corresponding temperature at the maximum was determined graphically and with a Gaussian fit to the data. The temperatures for these maximum hydrogen decomposition rates are listed in the last two column of Table 1. The peak hydride decomposition temperature varied from sample to sample, but ranges between 235°C to 332°C.

Table 1. Summary Results of Hydrogen Release From SNF in Vacuum

TGA Run #	Sample Characteristics			First Peak Hydrogen (wppm)	Temperature (°C) at max. H ₂ Release	
	ID	Weight (g)	Description		Expt. Data	Gaussian Fit
17	5-S1A-E1B	4.95	Sectioned from the corroded end of SNF 4378	18	332	323
24	10-S3-A1	6.35	Sectioned from the damaged end of SNF 4366	44	321	350
25	10-S3-F1	6.87		80	300	319
26	5-S1A-E4C	4.25	Sectioned from the corroded end of SNF 4378	72	290	295
27	5-S1A-E3B	5.47		38	235	237
28	5-S1A-E3C	3.64		38	265	263

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Figure 1. Schematic of the TGA/MS System

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Figure 2. A Plot of Hydrogen Intensity and Sample Temperature versus Time for TGA run 17.

Figure 3. A Plot of Hydrogen Intensity and Sample Temperature versus Time for TGA run 24.

Figure 4. A Plot of Hydrogen Intensity and Sample Temperature versus Time for TGA run 25.

Figure 5. A Plot of Hydrogen Intensity and Sample Temperature versus Time for TGA run 26.

Figure 6. A Plot of Hydrogen Intensity and Sample Temperature versus Time for (a) TGA run 27 and (b) A Rerun of TGA 27 using same sample.

Figure 7. A Plot of Hydrogen Intensity and Sample Temperature versus Time for (a) TGA run 28 and (b) A Rerun of TGA 28 using same sample

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A P P E N D I X B

HIGHLIGHT REPORTS COVERING SMALL SAMPLE FURNACE DRYING TESTS

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APPENDIX B

HIGHLIGHT REPORTS COVERING SMALL SAMPLE FURNACE DRYING TESTS

The following Pacific Northwest National Laboratory Highlight Reports are included in this Appendices covering the small sample furnace drying tests.

1. Description of Furnace Testing Apparatus, Walt Gray, John Abrefah, Tim Pyecha, and Steve Marschman--September 5, 1995.
2. ITA Process Drying and Conditioning Testing, John Abrefah, Walt Gray, and Steve Marschman--October 6, 1995.
3. IPS Conditioning of Corroded N Reactor Fuel from K West Storage Canister 4378, John Abrefah, W. Gerry, Walt Gray, and Steve Marschman--March 21, 1996.

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HNF-3534, Rev. 0

Description of Furnace Testing Apparatus

Walt Gray, John Abrefah, Tim Pyecha, Steve Marschman

The "furnace testing" apparatus is a test bed for performing drying and conditioning testing of spent nuclear fuel and sludge samples. The apparatus (shown schematically) was designed to accommodate a wide range of testing conditions. It is installed in the Postirradiation Testing Laboratory G-Cell (hotcell). The furnace is capable of heating to 1000 degrees C. It is controlled by a programmable controller capable of performing a wide range of heating/cooling cycles.

Samples are prepared and placed in a sample boat which is in turn inserted into a tube made of alumina or silicon carbide inside the furnace. Alumina tubes are used for drying/conditioning tests, while silicon carbide tubes are used for ignition testing. Tubes are available to accommodate samples ranging from a few cubic centimeters up to a section of an outer N-Reactor element 20 cm long.

The atmosphere within the furnace is controlled using the system's gas train. The gas train uses digitally controlled mass flow controllers to meter any conceivable mixture of gases into the system. A vacuum pump is provided to allow operation under less-than-atmospheric conditions. The furnace system was developed to operate between 1 and 6000 torr.

A gas chromatograph is provided to analyze the constituents in the gas stream. A moisture monitor is provided to provide real-time measurement of any water evolved from the test samples. Additionally, chemical water traps (columns containing Drierite) are also provided to capture all the water released from the samples.

A data acquisition system captures many different inputs for evaluation. Typically, we record the furnace and sample temperatures, system pressure, readings from the moisture monitor, and the mass flow of the gases used.

By mid August 1995, over six runs have been completed using this apparatus in the hotcells. We have performed the ITA conditioning cycle and the Cold-vacuum Drying (CVD) cycle to fuel samples from the middle of the "ugly" element. We are preparing to take samples from the damaged end of the "ugly" element and the "bad" element for further testing. The results of these tests will be reported in another highlight report.

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Last Updated: September 5, 1995

ITA Process Drying and Conditioning Testing

John Abrefah, Walt Gray, Steve Marschman

Experimental

Two spent nuclear fuel (SNF) specimens were subjected to the proposed Independent Technical Assessment (ITA) team drying and conditioning cycle in the furnace testing apparatus located in the Postirradiation Testing Laboratory (PTL) G-cell. Fuel specimens from the uncorroded mid-section of a corroded N-Reactor outer element taken from K-West Basin canister 4378 were used in these tests.

The heating cycle used for the conditioning cycle (basically the cycle proposed in the ITA study) consisted of the following:

- ☐ The furnace was purged at ambient temperature with high-purity argon (99.999%) and dried to a moisture content of about 1 ppm, after which the time-temperature-atmosphere conditioning schedule was imposed.
- ☐ A fuel drying step in which the SNF is dewatered (free water removal) at 373 K under dry argon for approximately 10 hours, then dried at 573 K under dry argon for approximately 24 hours (to remove water of hydration and partially decompose any uranium hydride present).
- ☐ A fuel passivation step, in which the fuel is exposed to a 98% argon-2% oxygen atmosphere at temperatures ranging from 423 K to 523 K for about 10 hours, to create an adherent, passive oxide film on any exposed uranium-metal surfaces. In the testing runs for this report, this step was conducted at near atmospheric pressure.

The off-gas from the conditioning tests was monitored for composition using a gas chromatograph (GC) to detect hydrogen and oxygen, and a moisture monitor to detect gaseous water. The total water release during the tests was collected (trapped) in a molecular sieve (Drierite) column and quantified by weighing the column before and after each test. The specimen temperature was monitored using a calibrated Type-K thermocouple connected to a digital readout.

Results

The specimen temperature, the hydrogen in the off-gas stream, the moisture concentration in the off-gas stream, and the oxygen concentration are shown in two plots. Figure 1 shows the results from the drying portion of the ITA cycle. Figure 2 shows the results from the passivation portion of the ITA cycle.

The results shown in Figure 1 indicate there was an increase in the moisture content for the first drying cycle during the transient heat-up of the specimens, and the hydrogen concentration was below the GC detection limit. During the second drying cycle, both hydrogen and moisture concentration peaked during the transient heat-up of the specimens. The moisture eventually decreased to the low detection limit of the moisture monitor, but the hydrogen leveled off at about 9 ppm in the off-gas stream. The total hydrogen release at the end of the second cycle was 0.1 mg; the total moisture was 0.3 mg. These values correspond to 2 ppm hydrogen and 5 ppm water in the specimens.

The results shown in Figure 2 point out the depletion of oxygen in the gas stream that occurs (as expected) during the passivation cycle. The total oxygen pick-up by the specimens is about 70 mg. The hydrogen and moisture concentration in the furnace off-gas, detected by the GC and moisture monitor, are also shown in the figure. Both the moisture level and the hydrogen concentration peaked during the transient heat-up of the specimens, similar to the observations during the drying cycle. The hydrogen concentration in the off-gas stream during this passivation cycle was lower than the amount observed during the drying cycle and it was also lower than the moisture concentration in the off-gas stream.

When the oxygen supply in the gas stream was turned off at the end of the cycle, the hydrogen concentration increased. The total amount of hydrogen observed during this cycle was 0.01 mg and the moisture concentration was 0.03 mg.

The before- and after-weights of the specimens (numbered SFEC5,4378-S2-H and J) show that the specimens lost about 181.6 mg and 180.2 mg, respectively. A black, powdery residue was found in the specimen holder after the second furnace testing. The residue, which weighed 0.6081 g, was collected and sampled for X-Ray diffraction (XRD) analysis. The presence of this residue could account for the weight loss by the specimens in the first two runs (about 712.9 mg) caused by spalling off the oxide layer during the passivation cycle. The XRD spectra identified the residue as mainly U_4O_9 phase.

A test was performed in which no specimen was placed in the furnace (i.e., a blank run). The results of that test show that only a small amount of moisture desorbed from other surfaces inside the furnace system and there was no detectable hydrogen measured. The oxygen pick-up by the rest of the furnace material was also insignificant.

Discussion

The results of the furnace testing indicate that moisture and hydrogen evolved from the fuel specimens. The probable sources of the observed moisture are (a) *absorbed* water in the oxide layer formed on the specimen during specimen-cutting operations; and (b) *surface adsorbed* water on the specimens. The hydrogen, however, could be from the following sources:

Dissolved hydrogen in the cladding;

Uranium hydride decomposition and/or reaction with moisture and/or oxygen;

Zirconium hydride decomposition and/or reaction with oxygen and/or water; and/or

Reaction of the uranium with moisture contained in the specimen and/or gas stream.

The low limit of solubility of hydrogen in uranium cannot account for the level of hydrogen measured, but still can contribute a small fraction to the amount of hydrogen measured. The depletion of the moisture source (Figure 1) even though hydrogen is being released, coupled with the moisture response of the system to the oxygen addition (Figure 2) seems to diminish the probability of uranium reactions with moisture as the hydrogen source.

The observation that both spallation occurred from each sample (i.e., weight loss by the specimens) shows that the 10-hour passivation time probably may be too long for oxidation at 250 °C, if the objective is to form a passivated, adherent layer. The XRD analyses of the residue show that the U_4O_9 phase is formed at this temperature instead of the anticipated UO_{2+x} . The formation of the higher oxide phases might be the cause of the oxide spalling since it is known that these phases are much less dense than the uranium metal fuel.

For the uranium specimens used in these tests, the calculated oxide thickness resulting from the passivation cycle is 40 microns (the density of uranium dioxide, 10.96 g/cm³, was used in the calculations; the density of U_4O_9 can vary from this by 1 to 5%); the total weight of the oxide layer is 295 mg. The calculations show that a loss of about 60% by weight of the oxide layer could account for the observed weight loss in the specimens.

HNF-3534, Rev. 0

**"Ugly" outer fuel element taken
from K-West canister 4378.**

Figure 1. Drying portion of the ITA drying/conditioning test

Figure 2. Passivation portion of the ITA drying/conditioning test

IPS Conditioning of Corroded N-Reactor Fuel from K-West Storage Canister 4378
J. Abrefah, W.G. Gerry, W. J. Gray, and S. C. Marschman

Corroded N-Reactor fuel specimens were cut from the damaged end of the outer fuel element removed from K-West storage canister 4378. Three specimens were subjected to the Integrated Process Strategy (IPS) conditioning process in the Furnace Testing Apparatus located in the Postirradiation Testing Laboratory. One sample was processed in Run #21, while two samples were processed in Run #23. The samples were cut using a tungsten-carbide saw under an argon cover gas. The as-cut samples are shown in Figures 1 and 2.

The IPS conditioning process consists of a cold-vacuum drying (CVD) cycle, a hot-vacuum drying (HVD) cycle, and a conditioning cycle. To simulate the environment that will exist in a freshly loaded and drained MCO, the fuel samples are dampened by adding between 3 and 5 mL of distilled water to the sample boat prior to being subjected to the CVD cycle. The samples were then cold-vacuum dried at a reduced pressure of about 38 Torr and a temperature of 50°C for about 10 hours. To insure that the system atmosphere would remain inert, high purity argon gas was fed in at a rate of 94 cc/min (a rate which would not overwhelm the vacuum pump). Following CVD, the temperature was raised to 300°C (at 38 Torr pressure) and held for 24 hours. The specimens were allowed to furnace cool to the ambient hotcell temperature following completion of the HVD cycle. The vacuum pump is also turned off at the end of the HVD cycle and the system is kept inert by continuing the flow of argon gas.

The start of the conditioning cycle is marked by the introduction of oxygen to the flowing argon cover gas. The mixture used is 2% O₂ and 98% Ar. The system pressure is maintained at about 1 atm (760 Torr). Once the oxygen baseline is established in the gas chromatograph (about 2 hours), the system is heated to 250°C and held for 10 hours. Following completion of the conditioning cycle, the furnace is turned off and the samples are allowed to furnace cool to the ambient hotcell temperature. The oxygen flow is also turned off at this time and the system is allowed to cool under flowing argon cover gas. It should be noted that in Run #21 the oxygen mass flow controller failed to shut off the flow of oxygen at the end of the conditioning cycle, which will be discussed further.

The results of Run #21 are shown in Figures 3 and 4, while Run #23 are shown in Figures 5 and 6. Figures 3 and 5 show the CVD and HVD portions of the tests, while Figures 4 and 6 show the results from the conditioning cycles. In each run the hydrogen and water present in the system atmosphere was measured; the oxygen was measured during the conditioning cycle of each run to determine the oxygen pick up rate by the sample.

The results shown in Figure 3 (Run #21) indicate that the water added to dampen the sample was easily removed within the first 1.5 hours. After 10 hours the temperature was increased to 300°C, and it is at this time that the majority of the free hydrogen that can be removed during HVD comes off the sample. Determination of the area under the hydrogen versus time curve yields 0.14 mg of free hydrogen removed from the sample during HVD. The hydrogen release peak occurred at about 261°C, and took about 27 hours to decay to near zero. Almost no water was removed from the sample during the HVD cycle.

The conditioning results shown in Figure 4 (Run #21) indicate a small quantity of water is released during the time period that the oxygen baseline is established in the gas chromatograph. This release (within the first one-half hour of the test) is due to adsorbed water on the surfaces of the oxygen gas line which is normally isolated from the system except during conditioning cycles. As the temperature was ramped to the 250°C conditioning temperature, very small quantities of hydrogen and water were

observed in the gas stream. The water release peaked at about 227°C, and the totaled 0.361 mg. The hydrogen observed totaled about 0.004 mg. These small quantities could be from oxygen reactions with uranium hydrides near the surfaces of the sample, or small amounts of water which will have become attached to the sample surface during the cool-down period between the HVD and conditioning cycles as a result of residual water in the high-purity argon. The sample picked up 134.5 mg of oxygen over the 10 hour conditioning cycle. During the isothermal conditioning cycle, the results show no indication of any barrier to oxygen pickup by the sample; the sample can continuously react with oxygen at a constant rate. As mentioned previously, the oxygen mass flow controller failed to shut off the oxygen flow at the end of the conditioning cycle. However, this provides additional information. The sample oxygen pickup decreased with decreasing temperature, and by 200°C the pickup is quite small. The oxygen pickup is nearly zero at 160°C. Thus, these results indicate that attempts to perform conditioning below 200°C would be impractical.

The results from the CVD and HVD cycles for Run #23 are shown in Figure 4. This test contained two specimens (one for use in a future ignition test). For this test the furnace was heated at a ramp rate not exceeding 2°C/min (while the ramp rate in Run #21 was about 10°C/min). The results are quite similar to those obtained from Run #21. Most of the added water was removed during the CVD cycle, and only a small amount was observed during HVD. Like Run #21, the hydrogen release peak occurred about 261°C, and decayed to near zero within 22 hours. The total hydrogen observed was 0.152 mg.

The conditioning results from Run #23 (shown in Figure 6) are also similar to Run #21. The furnace ramp rate was again controlled at 2°C/min, which was slower than Run #21 (10°C/min). The moisture and hydrogen releases were again very small. The specimens picked up a total of 174 mg of oxygen during the 10 hour conditioning cycle.

Several observations can be made from the results of these drying and conditioning tests on corroded. First, conditioning at temperatures below 200°C is impractical because the fuel did not take up much oxygen below this temperature. The corroded fuel picks up more oxygen than the uncorroded fuel (100+ mg as compare to about 30 mg for uncorroded fuel in Test #6¹). As in Run #21, the results show the kinetics of the oxygen pickup were linear. The corroded fuel also releases more hydrogen during the HVD cycle than the uncorroded fuel (0.1+ mg hydrogen as compared to 0.03 mg observed for undamaged fuel tested in Run #16¹).

¹ J. Abrefah, et al. K-Basin Spent Nuclear Fuel Characterization Report II, PNNL-10944, March 1996, Pacific Northwest National Laboratory, Richland, Washington.

Figure 1. As-cut test specimen SFEC5,4378-S1A-G which was removed from the damaged end of the element taken from K-West canister 4378. This sample was subjected to the IPS conditioning process in Test #21.

Figure 2. As-cut test specimens SFEC5,4378, S1A-B1 and -B2 which were removed from the damaged end of the element taken from K-West canister 4378. These samples were subjected to the IPS process in Test #23.

Specimen S1A-G Run #21

Figure 3. IPS CVD and HVD cycle results from Test #21. The CVD cycle covers the first 10 hours of the test, while the HVD covers the last 24 hours of the test at which time the furnace is shut down and allowed to cool.

Figure 4. IPS conditioning cycle results for the sample in Run #21.

Specimen S1A-B1 & -B2 Run #23

Figure 5. IPS CVD and HVD cycle results from Test #23. The CVD cycle covers the first 10 hours of the test, while the HVD covers the last 24 hours of the test.

Figure 6. IPS conditioning cycle results for the two samples in Run #23.

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